

DEPARTMENT OF THE INTERIOR

UNITED STATES BUREAU OF MINES
JOHN W. FINCH, DIRECTOR

INFORMATION CIRCULAR

ANNUAL REPORT OF THE NONMETALS DIVISION,
FISCAL YEAR 1937



BY

OLIVER C. RALSTON

AFTER THIS REPORT HAS SERVED YOUR PURPOSE AND IF YOU HAVE NO FURTHER NEED FOR IT, PLEASE RETURN IT TO
THE BUREAU OF MINES, USING THE OFFICIAL MAILING LABEL ON THE INSIDE OF THE BACK COVER.

INFORMATION CIRCULAR

DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

ANNUAL REPORT OF THE NONMETALS DIVISION, FISCAL YEAR, 1937^{1/}

By Oliver C. Ralston^{2/}

The nonmetallic minerals work of the Bureau of Mines started with the organization of the Mineral Technology Division in 1912. A special experiment station devoted to the mining, preparation, and processing of nonmetallic minerals was established in 1923 at New Brunswick, N. J., and concentration problems on nonmetallic minerals of all kinds also were studied at the Mississippi Valley Experiment Station at Rolla, Mo. In July 1936 the Nonmetals Division was organized, and in May 1937 the Nonmetallic Minerals Experiment Station at New Brunswick, N. J., was moved to and made a part of the new Eastern Experiment Station at College Park, Md.

At present the Nonmetals Division operates at three points: The Eastern Experiment Station, College Park, Md., which is headquarters for the division chief; the Southern Experiment Station, Tuscaloosa, Ala.; and the Northwest Experiment Station, Seattle, Wash., where coal washing and preparation studies are included with those on nonmetallic minerals. Sand, gravel, and aggregate work is carried on by the Mining Division, as sand and gravel preparation are intimately associated with mining methods. The Economics Branch of the Bureau of Mines also prepares occasional papers on nonmetallic technologic subjects in connection with the presentation of statistics on a particular industry and reviews of the mineral industry in foreign countries for use in the monthly publication, "Mineral Trade Notes."

CRACKING OF STEEL BY BOILER WATER^{3/}

Water is one of our most important nonmetallic mineral substances, and, while the total money spent on water may be less than that spent on oil, water is the more widely used. Boiler explosions, due to a variety of causes among which is the "embrittlement" of the boiler steel by certain waters used, present an important field for research on water treatment and preparation.

-
- 1/ The Bureau of Mines will welcome reprinting of this paper provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6974."
 - 2/ Chief engineer, Nonmetals Division, U. S. Bureau of Mines Eastern Experiment Station, College Park, Md.
 - 3/ Section on cracking of steel by boiler water was written by W. C. Schroeder, chemical engineer.

Before the investigation of intercrystalline cracking of boiler steel was started by the Bureau of Mines, it is probable that industry had spent approximately \$250,000 or \$300,000 over a period of 20 years on experimental study of this type of failure. Experimental results and data were collected from actual practice, but correlation was difficult, if not impossible, and in spite of this intensive study no real conception of the complexity of the reactions was obtained. This may have been due to the fact that the investigators tended to approach the study with the idea that only one or two variables were involved. For example, they believed that sodium hydroxide caused cracking in the presence of high stress in the metal and that certain substances would suppress the reaction.

As the study of the Bureau of Mines proceeded it was found that this was not true. The problem is almost as complex as that involved in the corrosion of metals, and the present investigation has necessarily divided itself into two distinct phases: (1) A study of the various solutions and conditions that would produce intercrystalline cracking and (2) a study of methods that would adequately prevent it.

Production of Intercrystalline Cracking

As a result of work carried out at New Brunswick during 1935-36, it was found that cracking could not be produced at 250°C. by sodium hydroxide solutions alone but that the solution must also contain a little sodium silicate. This discovery was so important that there was a tendency to assume that if the action of these solutions were thoroughly investigated it would be possible to correlate all the experimental and operating facts concerning embrittlement. The investigators tended to make the same assumption themselves. After the action of these solutions had been studied about 6 months, many observations could readily be correlated and fitted into a definite picture, but a few slight discrepancies still existed. Fortunately, at this time one of the test bombs developed a crack of a very peculiar nature and sharply focused attention on these discrepancies.

An intensive study then revealed that not one or two solutions or mixtures such as sodium hydroxide and sodium silicate produced cracking but that a whole series were capable of producing the same result. The exact compounds and concentrations depended on the temperature and other experimental conditions. Table 1 lists a number of compounds that will produce intercrystalline cracking in concentrated sodium hydroxide solutions boiling under atmospheric pressure and in solutions held at 250°C.

TABLE 1. - Chemicals that may be added to concentrated sodium hydroxide solutions to produce cracking at atmospheric boiling point and at 250°C.

50 g of NaOH per 100 g H ₂ O boiling at atmospheric pressure		25 g of NaOH per 100 g H ₂ O at 250°C.	
Chemical	Concentration, g/100 g H ₂ O	Chemical	Concentration, g/100 g H ₂ O
KMnO ₄	0.2	Na ₂ SiO ₃	0.1-1.0 or more
NaNO ₃	.2	TiO ₂	.5
Na ₂ CrO ₄	.05-.2	GeO ₂	.3
PbO	.2	SbCl ₃	.3

A solution of 50 grams of sodium hydroxide per 100 grams of water which contains lead oxide and boils under atmospheric pressure has been found very effective. It also lends itself well to use in the study of protective action of various compounds. At 250°C. the sodium hydroxide-sodium silicate solution still remains the one most active in producing cracks.

The sensitivity of the reactions is indicated by the fact that the various agents in the table that produce intercrystalline cracking at the boiling point will completely stop cracking at 250°C. Furthermore, if two of the compounds that produce embrittlement are mixed at the atmospheric boiling point, one of them will prevent the action of the other. For example, enough sodium chromate will prevent the production of intercrystalline cracks with lead oxide. This sensitivity appears to be related to the oxidizing or film-forming characteristic of these agents on the surface of the steel.

Furthermore, other substances may be substituted for the sodium hydroxide. For example, a sodium nitrate-manganese chloride solution will start cracks in specimens of cold-rolled steel within 1 hour after they are immersed in the solution and will crack a 5/16-inch section of boiler flange steel within a half day.

It is also interesting to note that the quantity of manganese chloride used in the solution is so low that it could almost represent impurity in a commercial grade of sodium nitrate. Sodium nitrate which is certified as pure (c.p.) is, however, entirely without influence in cracking the steel, whereas if it contains even as little as 0.05 percent of manganese chloride rapid cracking results.

Even stranger than the substitution of sodium nitrate for sodium hydroxide is the fact that the so-called "caustic" embrittlement can be produced by a very dilute nitric acid solution containing manganese chloride. The action of these acid solutions indicates how completely the ideas concerning the production of intercrystalline cracks have been revised.

As a result of the experimental work a theory has been developed which fairly well correlates the known facts. The mechanism involves formation of a protective layer on the steel which is not continuous enough to prevent the solution from attacking the grain boundaries. Such a coating may also be cathodic to the exposed or anodic grain boundaries, and electrochemical action will accelerate or increase the attack. In sodium hydroxide-sodium silicate solutions the silica has actually been found to deposit on the surface of the steel at 250°C. A solution that will cause intercrystalline cracking at this temperature will not necessarily produce the same effect at some different temperature, as the film-forming characteristic of the sodium silicate may change or the corrosive effect of the sodium hydroxide may change. Similarly, the agents that produce intercrystalline cracking at the atmospheric boiling point will not necessarily do so at

250°C. owing to the different oxidizing or film-forming action which they may exert at the higher temperature.

These new results and their explanation have broad and important implications with respect to the production of intercrystalline cracks in boilers. First, not only one solution but a variety of solutions of different compositions may promote failure. Secondly, as the reactions may be started or stopped by surface conditions on the steel they will obviously be extremely sensitive to small changes. For example, a boiler operating with little dissolved oxygen may not encounter trouble until the concentration is allowed to increase and possibly form a film that will promote intercrystalline attack. On the other hand, if the oxygen increases still further the attack may be stopped. Oxygen is merely used as an example; salts such as nitrate, silicate, etc., play an important part. This sensitivity to changes in conditions gives the study somewhat the complexity of the corrosion problem, and indeed in a number of aspects similarities are indicated. Third, since temperature and solution conditions must be accurately adjusted to produce cracking, it may occur only intermittently in a boiler. If this is true, water taken from a boiler after cracking will not necessarily indicate the conditions that produce intercrystalline failure. Fourth, some substances which are used to prevent cracking do so by changing or producing a new surface film on the steel, especially over the grain boundaries. Under certain conditions protection is effective, yet the very formation of a film may promote intercrystalline cracking if the conditions are changed. Fifth, the results show definitely that it is not necessary to have an applied load to produce cracking. The internal stresses resulting from cold work or other treatment will allow the solutions to attack the steel. Sixth, neither repeated stress nor corrosion fatigue necessarily play a part in the production of this type of failure.

Prevention of Intercrystalline Cracking

With the complete study that has now been made of the production of intercrystalline cracks, it is possible to investigate adequately various compounds that may prevent this difficulty.

It has been believed for a number of years that in boiler operation certain concentrations of sodium sulphate would inhibit the action of the solutions. This salt frequently has proved a satisfactory preventive in stationary boilers, but it has been found to be distinctly unsatisfactory in locomotive boilers. Experimental studies have determined the influence of sodium sulphate in various solutions and at different temperatures; it offers protection only under limited conditions.

As previously mentioned, certain oxidizing compounds such as sodium chromate and sodium nitrate will prevent the intercrystalline attack of sodium hydroxide-sodium silicate solutions, but these compounds may create cracking if conditions are changed or if they are present in too low concentrations. While oxidizing agents may be used to prevent embrittlement in boilers, their addition to the feedwater would be dangerous owing to possible production of

intercrystalline cracks and acceleration of corrosion or pitting. One or two inorganic chemicals have been found to offer some protection against embrittlement, but two groups of organic chemicals are much more effective. Fortunately, these organic chemicals are extremely low in price and are sometimes waste products so their use in boilers would not be attended by economic difficulties. It is hoped to develop a satisfactory means for using them in operation.

It must be remembered, however, that on the basis of the theory so far evolved, any protective agent may, under certain conditions, actually create embrittlement. This is especially true of the inorganic compounds that would tend to produce oxide or metallic layers over the surface of the steel. If a chemical can be found that produces a continuous nonpolar layer, it should offer the most satisfactory and least dangerous means of protection.

Future Investigation

Two real problems remain to be considered by further investigation. The first of these is additional tests of inhibiting compounds to determine the exact conditions under which they may be used. The second is a study of the "mechanism" of the action of dilute solutions in the production of cracks. So far the investigation of the embrittlement has been based on the assumption that cracking occurred through the action of concentrated solutions produced by evaporation of the boiler water in a capillary space or small opening. Studies in the production of intercrystalline cracking with dilute nitric acid may indicate that a dilute alkaline solution, even in the range of boiler-water concentrations, might have some influence. This problem is being studied thoroughly with the hope of being able to state definitely before the investigation is concluded whether or not the dilute solutions materially influence the production of intercrystalline cracks.

KYANITE CONCENTRATION AND PREPARATION

For several years the Southern Experiment Station has been engaged in a study of the concentration of kyanite ores, especially of the Southeast Appalachian area. Kyanite occurs from Alabama to Maine in schists, and numerous areas contain deposits of milling-grade ore which are of major magnitude. Nevertheless, American kyanites have not been popular compared with the Indian kyanites for many purposes. At first, it was thought that this was due to their impurity, but the preparation of exceedingly pure concentrates revealed that this was not the fact. Concentrates far purer than the Indian material were still refused by some buyers. The maker of brick and similar refractory shapes wanted coarse grog as the backbone of his shapes, so that the interstices could be filled with fine grog and then a plastic binder. Most of the American kyanites on burning are converted into weak grains that will not serve satisfactorily as grog, whereas Indian kyanite retains much of its strength. Following is an outline of investigations to determine how to concentrate American kyanites and how to make superior grog and other products from the concentrates. Details will appear in a bulletin yet to be prepared.

Kyanite ores from California, Arizona, Alabama, Georgia, Tennessee, South Carolina, and Virginia have been concentrated successfully by froth flotation and table agglomeration during this research. Work on fibrous ores from Colorado and New Mexico is unfinished. Commonly kyanite ores show bladed crystals, but some fibrous kyanite is known which resembles sillimanite and is frequently mistaken for it.

The common gangue minerals of kyanite are quartz, muscovite, biotite, garnet, oxidized iron minerals, and clay. The ore milled at Celo Mountain, near Burnsville, N. C., contains as many as 26 minerals, but this is unusual. Kyanite crushes into splinters and long shapes which are difficult to concentrate by any gravity process, in spite of the high specific gravity of the kyanite. This shape factor makes it necessary to lose a high proportion of the kyanite if a satisfactory grade of concentrate is made. Only the more blocky particles of the kyanite enter the finished concentrate. Consequently froth flotation and similar processes have proven more important. Virtually all kyanite ore can be concentrated by froth flotation to give a concentrate of over 90 percent purity with extractions of similar

magnitude. In fact, as high as 98 percent purity can be obtained with over 90 percent extraction.

Agglomerate tabling, which depends on filming kyanite selectively with suitable reagents, followed by addition of enough fuel oil to agglomerate the filmed material in preparing it for treatment on a concentrating table, has also proved practical. The "greased" kyanite particles and agglomerates are easily rafted off the table by the cross water to give high-grade concentrate and good extraction. Details of this and the flotation work will be included in the proposed kyanite bulletin.

As flotation concentrate is not acceptable to a brickmaker who requires grog aggregate of the refractory substance, A. Gabriel and J. E. Norman, at the New Brunswick Experiment Station, undertook the problem of converting finely ground kyanite into coarse calcined material. Raw coarse kyanite can be added to a fire clay of high shrinkage, and the expansion of the kyanite at its "inversion" temperature (about 1,400°C.) cancels the shrinkage. However, the coarse particles of kyanite after calcination are usually too weak to permit use of a very high percentage of kyanite. Fine kyanite can also be used for this purpose, but the practice has not been common. Moreover, in ungraded-kyanite fines enough voids are present for "internal" expansion so that the over-all expansion of a mass is less.

The usual binder for kyanite grog brick made from Indian kyanite is about 20 percent of refractory clay, but this practice was not regarded as satisfactory and a binder was sought which could be mixed with finely powdered kyanite to make bats for firing into a strong grog. The Bureau of Mines 12 years previously had done some work on binders for coarse kyanite and found that 10 percent magnesia had some virtue. This was tested and found workable except that the magnesia should be reduced to as little as 4 percent with kyanite fines and finely divided MgO . These mixtures had to be compressed to give satisfactory contact, and small briquettes were made. They fired to excellent material of almost porcelainlike hardness. However, the crushed and sized grog was found to be subject to the usual heat shock of magnesia. Substitution of talc for magnesia, in equal weights, gave a product which was not subject to heat shock but which did not possess the wet-working characteristics necessary in pressing shapes. Addition of about 2 percent of bentonite, in the face of the fact that its alkali content would act as a flux, gave enough plasticity to the mix, and there was no apparent loss in refractoriness. The resulting material gave excellent grog that would withstand well the 25 cycles of heating and chilling demanded in glass-tank block specifications. In fact, 35 cycles between 850°C. and room temperature were used as a test. As the bats fired for grog production were in the form of bricks their expansions were measured; it was found that this mix of kyanite flotation concentrate with 4 percent talc and 2 percent bentonite, fired at 1,650° to 1,700°C., would retain the same dimensions as the original pressed shape. This would make possible a kyanite brick of very high kyanite content and excellent heat-

shock characteristics if porosity could be kept low enough. Pressures of 10,000 pounds per square inch (on a 4-inch column) were adequate to keep ultimate porosity below 20 percent. Whereas the original objective was to prepare grog of high kyanite content, the ultimate result was brick of high kyanite content with satisfactory porosity and spalling resistance, which was produced without change in volume at one firing. Only with kyanite fines of the size of flotation concentrate is this possible. Details will be published in the proposed kyanite bulletin.

SPODUMENE CONCENTRATION AND LITHIUM EXTRACTION

A new process for drying air with concentrated solutions of lithium chloride was brought to the Bureau's attention. This salt is one of the most soluble salts known at ordinary temperatures (65 percent solutions), and these strong solutions have as little as 12 percent of the vapor pressure of pure water so that 12 percent relative humidity might be expected from washing air with them. When the available lithium chloride was used the process suffered from high installation costs, which could be lowered greatly by decreasing the cost of lithium chloride. Other uses of lithium chemicals were also found to be increasing and probably would expand greatly if the cost of lithium in its ores could be decreased.

Survey of the ores revealed that spodumene is the principal ore of reasonably high lithium content that is available in quantity; however, most of the spodumene ores are disseminated and require concentration. Huge reserves seem to be indicated in North Carolina and South Dakota, while numerous fair-sized occurrences are known in Maine and Massachusetts.

Although fine grinding and froth flotation gave fair results after gravity-concentration methods had failed, it was discovered that when spodumene is heated from 900° to 1,150° C. it alters to its beta form of crystallization which has much lower specific gravity and greater volume. This alteration so reduces the strength of spodumene granules that gentle mulling will convert them into fine powder which is easily separated from the unaffected quartz, feldspar, mica, and other minerals in the ore. The result was published^{4/} and has brought about active investigation of the possibilities of producing beta spodumene powder for chemical purposes and as a ceramic raw material. Being a lithium feldspar, the material promises to be a desirable substitute for feldspar both in the pottery and glass trades. Lithium is a more active flux than potassium, and not as much spodumene as feldspar should be needed for pottery. This permits the use of more quartz which adds toughness to a ceramic body. The translucence of the spodumene bodies already observed is higher at any one temperature than with feldspar. In glazes a mixture of spodumene and feldspar promises much owing to lower melting temperature and expansion characteristics. The T. V. A. ceramic laboratory is investigating this subject, and the promise of such mixtures emanates largely from that source and will be described in their publications.

^{4/} Fraas, F., and Ralston, O. C., Beneficiation of Spodumene by Decrepitation: Rept. of Investigations 3336, Bureau of Mines, February 1937, 13 pp.

Existing methods of extracting lithium from spodumene are expensive and cumbersome, therefore chloride volatilization was adapted to the problem. The final process comprised mixing calcium chloride and limestone with the spodumene and heating the mixture in a rotary kiln until cement clinker formed. The lithium is volatilized as lithium chloride, whose fumes can be captured after cooling the gases and passing them into a Cottrell precipitator. This work has now been published.^{5/}

The cement clinker formed should pay for part or all the calcium chloride, and if white cement is produced by using low-iron spodumene and limestone the whole operation might be performed without expense to the lithium chloride produced. As soon as use of lithium chemicals expands sufficiently to permit the use of this type of machinery the cost should be greatly lowered.

FROTH FLOTATION OF TREMOLITE-TALC MIXTURES

Cooperative work with the W. H. Loomis Talc Corporation, of Gouverneur, N. Y., was carried out during the winter of 1936-37 on separating talc and tremolite from the talc mines of the Adirondak region. Tremolite is related chemically to talc except that lime has replaced a part of the magnesium of the talc. In ceramics mixtures of talc and tremolite have been used to good effect, especially in tile bodies. The object of the work was to prepare purer talc for special markets and to control the talc-tremolite ratio during milling. Much of the talc in these ores is fibrous, although some foliated talc is present. The latter, if separated, is especially desirable in other markets than ceramics, paint, and rubber filler. All objectives were reached. Talc is a natural floater, and many different reagents will float it. The real problem seems to be one of depression. Other minerals if rubbed with talc take on a talcose coating and must be depressed or dispersants or detergents added to clean the coated minerals. This theory was evolved during the work. The best collectors discovered were DP 243, a cationic reagent manufactured by Du Pont, diamylamine, and the nitrogenous bases extracted from petroleum acid sludges by the Shell Oil Co. in its California plants. An acid circuit, especially during cleaning, is preferred to a neutral circuit. Pine oil or the higher alcohols were acceptable as frothers. Pine oil without any other reagent gave good results on one of the ores from this area. Details will be published in a future publication.

EFFECT OF TEMPERATURE ON STRUCTURE OF SOAPSTONE

At the Northwest Experiment Station samples of soapstone from a deposit in the Cascade Mountains of Washington were heated to various temperatures, draw trials were made, and the effect of temperature on the structure and texture was studied microscopically. The results obtained

^{5/} Fraas, F., and Ralston, O. C., Chloride Volatilization of Lithium from Spodumene: Rept. of Investigations 3344, Bureau of Mines, May 1937, 11 pp.

indicated that the talc changed to enstatite at about 1,000°C. and changed further to clinoenstatite at about 1,200°C. At higher temperatures iron impurities united with silica, probably to form fayalite along the original impure schistose planes of the soapstone. A manuscript on this subject has been completed and submitted for publication.^{6/}

REFRACTORY PROPERTIES OF CHROMITE IN THE PACIFIC NORTHWEST

The Northwest Experiment Station of the Bureau of Mines has studied many of the available chromites of the Pacific Northwest. Deposits in Washington and Oregon were sampled and tested. The Montana low-grade chromites are being studied at the Montana School of Mines and therefore were not sampled. Good chromite has a P. C. E. value of above cone 38, and most of the chromites studied were above cone 35. Olivine is the principal gangue mineral, as the chromites occur in dunite intrusions. Other altered magnesium silicates were also observed. On heating, the first glass forms at about cone 20 and vesicular structures form at cone 26. Most weight and volume losses occur between cones 26 and 35, and recrystallization of the gangue mineral was noted above cone 30 but decreased at cone 40. The gangue was visible only in thin films around the chromite grains after firing to the highest temperature. Clinoenstatite was one new crystal recognized in the films after firing, but mineralogical investigation has not been completed. Mixtures of olivine and chromite should show a fusion eutectic with 80 percent olivine at cone 35, but 30 percent olivine was necessary to change the P. C. E. of chromite. Kaolin is a much more violent flux for chromite. Work is continuing on these chromites.

PROPERTIES AND USES OF OLIVINE IN THE PACIFIC NORTHWEST

A second year's work on this subject has now been completed at Seattle. Great dunite areas have been visited and sampled for their olivine-bearing rock. The fluxing effect of several oxides on olivine was determined by the cone-fusion method. Alumina, ferric oxide, and boric oxide are important fluxes but chromite up to 50 percent had a neutral effect.

Olivine grain was also tested for a blast sand on account of its hardness, which is close to that of quartz. The vitreous dunite from the Twin Sisters Mountains gave a friability index equivalent to that of the no. 2 blast sand from California but was reduced much more in size than Ottawa sand.

Preliminary tests on olivine grains as a molding sand were quite favorable. Further work is contemplated, and a publication is planned.

^{6/} Wilson, Hewitt, and Pask, J. A., The Effect of Temperature on the Structure of Soapstone: Manuscript submitted to Am. Ceram. Soc.

HYDRATION OF LIME

The effects of conditions of hydration and prior burning on the properties of lime hydrate were studied. Both high calcium and dolomitic limes were carefully burned and then hydrated in a special apparatus designed for close control of the quantity of water added and the temperature of hydration (by water cooling). The various hydrates were tested for settling rates, putty volumes, and plasticity index (Emley plasticimeter.) The most important variables discovered were temperature of hydration and degree of hydration of the magnesia in the hydrated product. The better the hydration of the magnesia, the higher the plasticity index. Dolomites that at present do not yield finishing limes could be made to do so by controlling conditions during hydration.

SIZE ANALYSIS OF MINERAL POWDERS

Mineral powders usually have been analyzed in the subsieve range by wet methods. The use of dry air for this purpose has many advantages. An apparatus for fractionating fine powders has been developed in which effective use is made of a stream of air. The range of application of the apparatus, in which analysis is based on Stokes law of particle fall, has now been extended to cover ceramic mineral powders such as feldspar, flint, talc, pyrophyllite, and china clay.

Law of Particle-Size Distribution

A mathematical study was made to provide a more convenient method of comparing the results of size analyses of mineral powders, and a relatively simple expression was found which satisfactorily reproduces the relationship between natural and artificially prepared powders. The data can be expressed in the form of statistical constants of surface area, number of particles, and coefficient of uniformity. These are true integral values to be distinguished from crude increment values often calculated. The law was tested on ceramic materials, cements, hydrated lime, soils, paint pigments, and clays that had been accurately sized. Now that it has been published the Roller law of particle-size distribution will undergo its final tests in the hands of other experimenters to see if it has as wide a range of application as might be wished.

RELATIVE VALUE OF GYPSUM AND ANHYDRITE IN CEMENT

Large quantities of gypsum are used as an addition to portland cement. This mineral contains, as a rule, various quantities of the mineral anhydrite. The question of the usefulness of anhydrite has been the subject of much controversy.

A study of the relative value of these minerals in cement has been concluded. It was found in this study that cement exists in different states of activity, depending on the amount of adsorbed water vapor. Curiously, while a small amount of water vapor depresses the setting of cement, an excess reactivates the cement.

In the study freshly ground cements were artificially conditioned by causing them to adsorb as much water vapor as they would adsorb inadvertently in practice.

It was found that anhydrite is intrinsically less effective than gypsum as a retarder of setting. The amounts that may be used safely depend on the conditioning of the cement. As much as 75 percent of anhydrite associated with gypsum may be effective, but in practice the amount that may be used safely is less. The compressive and tensile strength appear to be lowered slightly by the presence of anhydrite.

POZZOLANIC MINERALS

A type of mineral that has been known for several milleniums is the pozzolanic minerals or "puzzolans." Roman structures made with lime and volcanic ash 3,000 years ago are still standing. Recently, admixtures have been made to cement which unite with the lime liberated during the setting of the cement and thus add to the cement materials normally present. In the larger dams and other structures built in the West in recent years a certain addition of pozzolanic mineral has been specified. Cement mortars can, under correct conditions, be made more plastic, more impermeable, noncorrosive, and even stronger by including pozzolanic admixtures. With this in mind, a study has been undertaken of natural, artificial, and artificially enhanced pozzolanic minerals. Their true action is still obscure, and both scientific and technologic studies are needed. A better measure of workability or plasticity of mortars is needed, and a tentative one has already been devised and will be reported later as the first step in the study of pozzolanic minerals.

REFRACTORY CRUCIBLES OF NONPLASTIC MATERIALS

Improved superrefractory crucibles of such materials as magnesia, zirconia, alumina, and thoria were made by multicompression at a series of independent pressures, gaged according to the zone and orientation of the part of the crucible being formed. A description has been published.

QUARTZ AND SILICA IN WASHINGTON

The Northwest Experiment Station in cooperation with the College of Mines, University of Washington^{1/} reviewed the geologic literature of the State of Washington for mention of possible indications of highly siliceous rocks and minerals. Geologic maps of the important districts have been copied. Samples have been collected from all parts of the State and tested for iron and silica content, pyrometric-cone-equivalent value, refractoriness, melted color, and abrasion resistance, and attempts have been made to concentrate the quartz content by simple washing, tabling, flotation, and magnetic separation. The study can not be complete because vast areas of the State are unknown and inaccessible mountains and forests.

^{1/} The Works Progress Administration, Project 641, furnished two of its employees to assist in this study.

The interesting rocks include the quartzites in the old metamorphic rocks of pre-Tertiary age that outcrop as an extension of the Belt series along the Idaho border and in Stevens, Ferry, Okanogan, Chelan, Whatcom, San Juan, Skagit, Snohomish, King, and Kittitas Counties. The quartzite sand from one series in Stevens County is already in use in Seattle. Vein quartz is found in Stevens, Pend Oreille, Whatcom, Skagit, Chelan, and Pierce Counties and has been used to some extent in silica brick, pebble dash, and pulpstones. The large masses of granodiorite in the northern part of the State have contributed, since Cretaceous times, to the formation of enormous thicknesses of sandstone. In a few places, such as near Spokane and Wenatchee, the quartz content is high and the ferromagnesium and feldspar impurities are low, but the vast majority of the Eocene and younger sandstones of the Swauk, Chuckanut, Puget, and other formations in southwestern Washington contain from 50 to 85 percent of silica and 1.5 to 7.0 percent iron oxide. The mineral composition of two typical washed Tertiary sandstones, made from a comparison of petrographic and chemical analyses, was as follows:

	A	B
Quartz	84.7	64.8
Feldspar	12.1	29.2
Muscovite	3.0	2.3
Biotite	Trace	.2
Andesite glass	—	1.5
Garnet	Trace	.2
Calcite	—	.3
Pargosite	—	.1
Glaucophane	—	.5
Iron minerals	<u>.1</u>	<u>.8</u>
	99.9	99.9

The sandstone often appears to be crushed granodiorite rock with little alteration. These sandstones have been used for building stone and for low-temperature, iron-foundry service.

Although the glacial sands of the Puget Sound region and the basalt sand of eastern Washington are of great value for highway and building construction, they have not been considered in this study because of their low silica content. The cement companies are seeking siliceous materials for the high, early-strength cements as those used in the Grand Coulee and Benneville Dams. The local bottle-glass company and the steel foundries wish to replace the Belgian sand with local materials.

The materials of highest purity are the quartz sands washed from the kaolins of the Spokane district near Mica, Wash., and the vein quartz. The former require additional table concentration to remove iron minerals and muscovite. Their freight rate to the Pacific Coast is \$3.90 per ton. They cannot be used for foundry or abrasive sand because of grain fragility but are more suitable for glass, potter's flint, and ceramic glazes. The cost of mining vein quartz, reducing it to the proper sand size, and treating

it for iron contamination from the grinding machinery handicaps this pure material in competition with Belgian sand.

The second group which contains 90 to 97 percent silica and 0.5 to 2.0 percent iron oxide includes the Stevens County quartzite sands and the Wenatchee sands of the Swauk formation. These are not pure enough for the best grades of glass but possibly can be used for amber and colored glasses. They show better possibilities for abrasive and foundry service, and large quantities of both have been tried successfully in iron and steel foundries. Concentration methods can be used to separate minute quantities of iron minerals, but most of their iron contamination occurs as surface and interior stain.

The impure Tertiary sandstones comprise the third group. Some of these can be used for low-temperature iron-foundry service, possibly for amber glass where the feldspar content is low, and for white building sand, as the common glacial and basalt building sand is very dark, but they are not tough enough for abrasive purposes.

Data have been collected on the occurrence of diatomite in Washington, Oregon, Idaho, and British Columbia.

FRACTIONATION OF CLAYS BY FROTH FLOTATION

A clay containing only one mineral is a rarity; however, owing to the difficulty of separating the minerals that constitute a clay, each assemblage has been more or less accepted as inevitable. Magnetic minerals could be removed by magnetic separators, and the granular material could be separated easily from the "colloidal" part by deflocculation and sedimentation. Fractional sedimentation in centrifuges has also been under investigation in recent years. Froth flotation is known to be mineralogically selective, but it also suffers from the tendency of the smaller minerals to float first.

An investigation to determine the amenability of clays to froth flotation has been in progress at the Southern Experiment Station for about a year and a half. The first work was undertaken in cooperation with the Tennessee Valley Authority in connection with their study of the possibility of utilizing North Carolina kaolin in the manufacture of porcelain. Certain impurities such as mica that could not be rejected by the most careful application of the deflocculation-sedimentation process were thought to be objectionable. Flotation offered the possibility of separating the clay minerals on a mineralogical rather than physical basis as in the usual practice. The crude North Carolina kaolin is mainly "clay substance", kaolinite, feldspar, mica, and quartz. The results of the work showed that the clay minerals can be floated from the gangue minerals. The order of floatability was "clay substance" (halloysite?), kaolinite, mica, and either feldspar or quartz, depending upon the procedure. The cationic reagents were used together with conditioning agents and a frother. The floated clay after treatment in a colloid mill was made into a satisfactory porcelain casting slip, and the porcelain was of excellent quality. Clays that were

not treated in the colloid mill were difficult to cast under the same conditions. Recently the work has comprised floating of the coarse kaolinite, much of which is lost and left in the residues of the deflocculation-sedimentation process, and determining the conditions for its use. So far little work has been done on clays other than kaolins.

CONCENTRATION OF FELDSPAR ORES BY FROTH FLOTATION AND AGGLOMERATE TABLING

The feldspar minerals are used in the glass and ceramic industry for alkali or alumina content or both. The requirements as to the proportion of alkalis are quite flexible, but the trade demands certain constant ratios of alumina to silica. Careful mining, blending, and hand-picking are used to maintain certain grades. To minimize the loss in the fines not amenable to hand-picking and to treat lower-grade ores that require grinding for liberation, various methods of beneficiation have been considered. The feldspar producers are not the only ones interested in a suitable means of purification, as some of the granite producers realize that they have a loss in the fines that may be turned into a profit. The physical properties of the feldspar and quartz are so nearly the same that some other method besides gravity concentration must be used. Furthermore, size requirements have a bearing on the adaptability of the process. Last year some work on the beneficiation of feldspar products was done at the Southern Experiment Station in connection with the study of the flotation of clay. Two methods of concentration were used - froth flotation for fine material and agglomerate tabling for minus 20-mesh material. Numerous products containing various kinds of feldspar were tested. Both methods are adaptable to the concentration of feldspar. By controlling the reagents either the feldspar or quartz can be separated from the other. Further work is in progress along these lines. It is too early to write papers on the subject, but encouraging results have been obtained. In the coming year it is expected to bring about a commercial separation of quartz and feldspar.

MICA SEPARATION BY FRICTIONAL ELECTRICITY

A research begun on pyroelectric separation of minerals, especially mica, has brought out the fact that mica separation by this supposed effect is actually a separation by frictional electricity generated by mica flakes sliding down glass shelves. A slide of long distance is not needed, and whereas glass shelves 6 inches long were used at first the size was later cut to 1.5 inches. The charged mica sticks at the lower edge of the glass, while the trajectory of quartz and feldspar grains carries them onto the next glass shelf. Variations and improvements are necessary to remove all of the mica in one treatment but with several treatments it has been possible to remove completely muscovite mica from a crushed and dried graphic granite.

COOPERATIVE INVESTIGATION OF RED IRON ORES

An investigation of the concentration of red-iron-ore has been carried out at the Southern Experiment Station in cooperation with the Republic Steel

Corporation. This investigation resulted from a study of the problem made about 5 years ago. At that time a system of gravity concentration was developed using small laboratory equipment. The results of the work were published in a Bureau of Mines Report of Investigations. The Birmingham district contains vast quantities of red iron ore which is so highly siliceous that it cannot be used profitably in the blast furnaces in its natural state. The ores which are of satisfactory grade are being depleted rapidly, and it will be necessary in the near future for some of the companies to draw on the more siliceous ores which will require beneficiation prior to smelting in the blast furnaces. Thus the problem of concentrating the red iron ores is of vital importance to all blast-furnace companies in the Birmingham district. The purpose of recent tests, made with equipment of semicommercial size, was to obtain more reliable information as to what results might be expected on a commercial-plant basis. A 2-ton sample of high-silica red ore was run through the equipment, and the results were quite satisfactory. The concentrates had about 2 percent less iron than those obtained in the previous small laboratory tests, but the recovery of iron from the original ore was about 2 percent higher. As a result of these tests the cooperating company is giving serious consideration to the building of a commercial plant.

Investigations on Coal-Washing and Preparation

The research on the preparation and washing of coal is conducted at the Northwest Experiment Station, at Seattle, Wash., and the South Experiment Station, Tuscaloosa, Ala., of the Bureau of Mines, under the direction of the Chief Engineer of the Nonmetals Division, but for convenience of readers of the Bureau's publications, the report of this work is given in the annual report of the Bureau's investigations on coal.

PUBLICATIONS OF THE NONMETALS DIVISION DURING 1936-37

Nonmetallic Minerals Experiment Station, New Brunswick, N. J.
(now known as the Nonmetals Division, Eastern Experiment Station,
College Park, Md.)

- BERK, A. A., AND SCHROEDER, W. C. Apparent Correlation between the Over-all Reaction of Solutions on Steel and the Embrittlement of Steel. Private printing, Am. Soc. Mech. Eng., New York.
- DAVIDSON, J. M., BERK, A. A., CONLEY, J. E., AND PARTRIDGE, E. P. Relation between Calcination Conditions and Extraction Behavior of Polyhalite. Ind. Eng. Chem., April 1937, pp. 478-482.
- FRAAS, F., AND PARTRIDGE, E. P. Potash from Polyhalite by Reduction Process (III). Ind. Eng. Chem. 28, August 1936, pp. 956-962.
- RALSTON, O. C. Resume of Work of the Nonmetals Division. Ceram. Age, vol. 29, no. 4, April 1937, pp. 116-117, 127-128.
- RALSTON, O. C., AND STERN, A. GEORGE. Resume of Work of the Nonmetals Division - Calendar Year 1936. Information Circ. 6934, Bureau of Mines, March 1937, 12 pp.
- ROLLER, P. S. Law of Size Distribution and Statistical Description of Particulate Materials. Jour. Franklin Inst., vol. 223, no. 5, May 1937, pp. 609-633.
- Size Distribution of Ceramic Powders as Determined by a Particle-Size Air Analyser. Jour. Am. Ceram. Soc., vol. 20, May 1937, pp. 167-174.
- ROLLER, P. S., AND HALWER, M. The Relative Value of Gypsum and Anhydrite as Additions to Portland Cement. Tech. Paper 578, Bureau of Mines, 15 pp.
- ROLLER, P. S., RITTENBERG, D. AND GABRIEL, A. Preparation of Laboratory Refractory Crucibles. Ind. Eng. Chem., Anal. ed. 8, Nov. 15, 1936, p. 486.
- SCHROEDER, W. C., BERK, A. A., AND PARTRIDGE, E. P. Effect of Solution Composition on the Failure of Boiler Steel Under Static Stress at 250° C. Proc. Am. Soc. Testing Materials, vol. 36, pt. II, 1936, pp. 721-754.
- Use of Solubility Data to Control the Deposition of Sodium Sulfate or its Complex Salts in Boiler Waters. Proc. Am. Soc. Testing Materials, vol. 36, pt. II, 1936, pp. 755-769.

Papers Presented at Meetings of Technical Societies

- RALSTON, O. C. Froth Flotation and Agglomerate Tabling of Nonmetallic Minerals. Presented at the meeting of the Canadian Institute of Mining and Metallurgy in March 1937 and to be published in the proceedings of that institute.

ROLLER, P. S. Classification of Methods of Mechanical Analyses of Particulate Materials. Presented at the meeting of the American Society for Testing Materials in June 1937 and to be published in the proceedings of the A. S. T. M.

SCHROEDER, W. C., BERK, A. A., AND O'BRIEN, R. A. Intercrystalline Cracking of Steel in Aqueous Solutions. New Experimental Work Forces a Broad Viewpoint. Presented at the meeting of the American Society for Testing Materials in June 1937 and to be published in the September 1937 issue of Metals and Alloys.

Northwest Experiment Station, Seattle, Wash.

SKINNER, K. G. Coke-Carbon Dioxide Relations. Ind. Eng. Chem., vol. 29, June 1937, pp. 696-697.

WILSON, H., AND MIDDLETON. Purification of Kaolin - Classification of Quartz and Muscovite. Jour. Am. Ceram. Soc., vol. 20, April 1937, pp. 126-135.

WILSON, HEWITT, AND SKINNER, K. G. Equations and Quadrant Charts for Determining the Heat and Air Requirements of Driers. Jour. Am. Ceram. Soc., vol. 20, April 1937, pp. 99-111.

—— Occurrence, Properties, and Preparation of Limestone and Chalk for Whiting. Bull. 395, Bureau of Mines, June 1937, 160 pp.

YANCEY, H. F. Program of Coal Research, Northwest Experiment Station, U. S. Bureau of Mines, and College of Mines, Univ. of Washington. Coal Age, vol. 42, 1937, p. 83.

Publications in Press

BERKELHAMER, L. H., AND WILSON, HEWITT. Abstract of Olivine as a Refractory Material. Submitted to the Geological Society of America.

WILSON, HEWITT, CHALK AND WHITING. To be a chapter of the Industrial Minerals volume of the Am. Inst. Min. and Met. Eng.

—— Mineral Pigments. To be a chapter of the Industrial Minerals volume of the Am. Inst. Min. and Met. Eng.

WILSON, HEWITT, AND PASK, J. A. The Effect of Temperature on the Structure of Soapstone. Submitted to the Journal of the American Ceramic Society.

YANCEY, H. F., AND GEER, M. R. Performance of a Baum-Type Coal-Washing Jig. To be published as a Bureau of Mines Report of Investigations.

To be Mimeographed by the Secretary, North Pacific Section,
American Ceramic Society, Seattle, Wash.

CLINE, R. W. Occurrence, Properties, and Uses of Olivine.

I. C. 6974

HURST, T. L. Chromite in Washington.

SKINNER, K. G. A Brief Discussion of Electric Tunnel Kilns and Charts for Computing the Relative Costs of Different Fuels.

Southern Experiment Station, Tuscaloosa, Ala.

COE, G. D., AND GANDRUD, B. W. Washability Studies of the Henry Ellen Bed at Acmar No. 5 Mines, Acmar, Ala. Rept. of Investigations 3315, Bureau of Mines, November 1936.

Publication in Press

HERTZOG, E. S. The Rapid Analysis of Barite Ores Containing Calcium Fluoride, without the Use of Fusions. Submitted to Industrial and Engineering Chemistry.